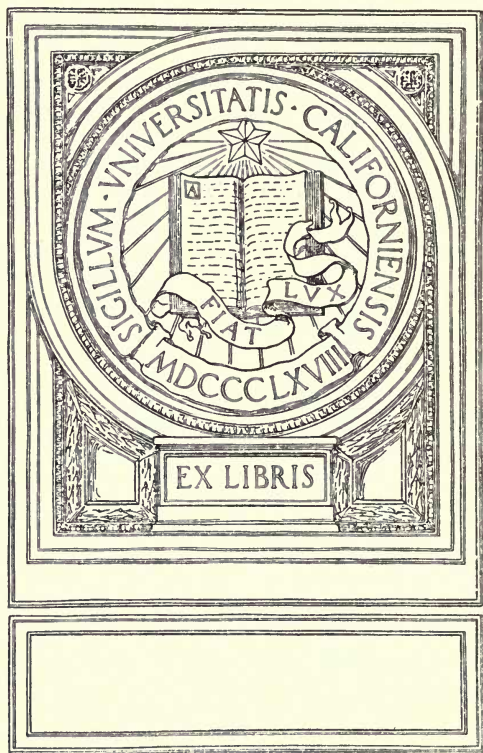


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A SHORT INTRODUCTION TO
THE THEORY OF
ELECTROLYTIC DISSOCIATION

A Short Introduction to The Theory of Electrolytic Dissociation

BY

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GENERAL

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CHAPTER I.

THE CONDITION OF DISSOLVED SUBSTANCES.

§ 1. *Diffusion of Gases.*—The apparatus represented in diagram 1 consists of two glass vessels of equal volume connected by a glass tap, C. A contains oxygen gas, and B is vacuous. According to the kinetic theory, the oxygen molecules constantly bombard the walls of A. The molecules are in a state of continuous and rapid motion, and the summation of their continuous and rapidly succeeding impacts on the containing walls constitutes the pressure which the gas is known to exert on them.

As long as the tap C cuts off communication between A and B, none of these travelling particles are able to enter B. When the tap is so turned as to connect A and B, there is a rush of gas into the latter. Numbers of the moving molecules find their way through the passage into B. In B they continue their motion—producing pressure on the walls of B, and tending (when their line of motion is in the right direction) to re-enter A. As long as A



FIG. 1.

contains a larger number of molecules than B, a larger proportion will leave A for B than B for A. The process of constant interchange continues, until the numbers of molecules in the two compartments are equal. The amounts of gas in the two compartments then remain equal, since in both cases the exports and imports balance one another. The gas diffuses until its concentration (mass of gas per unit volume) is constant throughout the whole space A B.

If B contains nitrogen gas instead of being vacuous, then both gases concentrate themselves uniformly throughout the enclosed space. The molecules of each gas pass between A and B as if the other gas were not present—with the exception of the very slightly impeding effect of collisions between the two species of molecules.

If A and B have different volumes, kinetic equilibrium is still obtained between the gases in A and B; and, as before, the concentration of either gas becomes and remains constant throughout the whole space.

Avogadro's Law states that, at the same temperature and pressure, equal volumes of gases contain the same number of molecules. The concentrations of the gases may thus be stated molecularly. Each gas, then, diffuses through the other until every unit volume throughout the space A B contains the same number of its molecules,

§ 2. *The Evaporation of Water.*—In Fig. 2, B represents water enclosed in a glass tube, A. Evaporation from the surface of B takes place, and water vapour enters the space above. According to the kinetic theory, some of the moving molecules of water escape through the surface of the liquid into the upper air. These continue their movements, and in course of time re-enter the liquid. As long as more particles leave the liquid than enter it, the amount of water vapour in the air steadily increases. A condition of kinetic equilibrium is finally obtained, when, in any given time, as many particles leave the air as enter it. The air is then saturated with water vapour, and the space above the water may be regarded as a solution of water in air. It exhibits the characteristic feature of solutions, *viz.*, diffusion of the dissolved substance until it is uniformly concentrated throughout the solution.

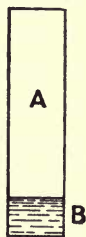


FIG. 2.

§ 3. *Sublimation of Camphor.*—If camphor takes the place of the water, similar results are obtained. Camphor particles enter the air, and a continuous process of interchange takes place between the solid and gaseous camphor. Finally, a state of balance is arrived at, and a saturated solution of camphor in air is obtained. The solid camphor may deposit all over the tube surface. Here, again, diffusion results in constancy of concentration throughout the solution.

Similarly, the gases in § 1 may be regarded as dissolved in one another. In the same way, air may be regarded as a solution of oxygen in nitrogen. Atmospheric oxygen is practically uniformly concentrated throughout the air. Accurate experiments appear to indicate that this is not absolutely the case, but the differences detected are very small.

§ 4. *Solution of Sugar in Water.*—If sugar takes the place of the camphor in Fig. 2, no solution of the sugar in the air can be detected. Theoretically, it may possibly be supposed to sublime in very minute quantities, but practically it is completely non-volatile.

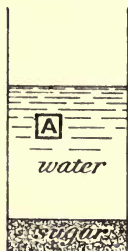


FIG. 3.

It behaves towards water, however, as the camphor behaves to the air. Its particles steadily diffuse through the water, and, finally, balance is obtained when as much sugar leaves the water for the sugar as leaves the sugar for the water in a given time. The water becomes saturated with sugar as the air becomes saturated with camphor, and the concentration of the sugar throughout the solution becomes and remains uniform by diffusion of the sugar particles. The process is slower in the case of the sugar—hence the custom of stirring dissolving substances to facilitate complete solution.

As in the case of the oxygen gas concentrating its molecules uniformly throughout the space in which

it is enclosed, so the saturated solution of sugar contains an equal number of molecules per unit volume. If, at any moment, the space A contains a larger number of molecules than any other equal space, a larger number of sugar particles will diffuse out of A than into it, until equilibrium is obtained. This uniformity of concentration secured by diffusion is characteristic of solutions.

The water is here regarded as affording a space throughout which the sugar molecules can diffuse, but it is obvious that the solvent plays an important part in the act of solution.

§ 5. *Pressure Exerted by Gases.*—According to Boyle's Law, the pressure exerted by a particular mass of oxygen varies inversely with its volume. If a particular mass, M , of oxygen occupy a particular volume, $2V$, it exerts on the containing vessel a certain pressure, P . On halving the volume—as by pushing in a piston until the space occupied becomes V —the pressure becomes $2P$.

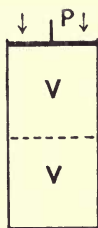


FIG. 4.

$$2V \times P = V \times 2P.$$

Since its concentration is now double its original value (having changed from $\frac{M}{2V}$ to $\frac{M}{V}$) the pressure remains proportional to its concentration—

$$P \div \frac{M}{2V} = 2P \div \frac{M}{V}.$$

The pressure of any mass of oxygen, then, is proportional to its concentration. From the molecular point of view, the gas pressure is proportional to the concentration of its molecules. Each molecule may be regarded as making a definite contribution to the gas pressure; and the total pressure, being the summation of all these contributions, varies directly with the number of gas molecules in unit space. The various deviations from Boyle's Law may be here disregarded.

The pressure of any mass of air enclosed in a space is the sum of the pressures exerted by the oxygen and nitrogen respectively. Regarding the nitrogen as dissolved in the oxygen and neglecting the pressure exerted by the latter, we may regard the pressure of the dissolved nitrogen as related to the concentration of its molecules.

It should be remarked that the pressure exerted by a gas mixture does not exactly obey the law of the sum of their pressures. Moreover, the solution of nitrogen in oxygen differs in certain respects from such a solution as that of salt in water. At a certain temperature, a definite mass of water can only dissolve a definite mass of salt, while nitrogen is miscible with oxygen to an unlimited extent.

§ 6. *Effects of Dissolved Substances on the Freezing and Boiling Points.*—In a similar way, certain effects due to solids dissolved in water are proportional to the concentrations of their molecules, *i.e.*, to the

number of molecules in unit mass of the solvent. This is true, for example, of the depression of the freezing points and of the raising of the boiling points of aqueous solutions of ordinary non-volatile solids.

It is well known that the addition of salt to snow will cause it to melt. This implies that the freezing point of the resulting solution of salt is below that of pure water. The same solution of salt can easily be shown to boil above 100° C. by introducing a thermometer into the boiling liquid. Similarly, aqueous solutions of cane-sugar and glucose freeze and boil less easily than pure water.

Cane-sugar and glucose have the respective formulæ of $C_{12}H_{22}O_{11}$ and $C_6H_{12}O_6$. Their molecular weights are therefore 342 and 180 (using round numbers for atomic weights), and 342 grammes of cane-sugar contain the same number of molecules as 180 of glucose. If 342 grammes of cane-sugar and 180 of glucose are dissolved respectively in the same masses of water so as to form dilute solutions, these two solutions have the same boiling and freezing points.

Thus, if gramme-molecular weights—342 and 180 grammes being the molecular weights of cane-sugar and glucose expressed in grammes—of these two substances are dissolved in 10 litres of water, the freezing points of the two solutions will be about 0.186° C. less than the freezing point of pure water.

Every molecule of cane-sugar therefore produces the same difference in the freezing point of a certain mass of water as a molecule of glucose. The above solutions boil at about 0.052° C. above the boiling point of pure water; and, therefore, an equal number of molecules of either cane-sugar or glucose raises the boiling point of a certain mass of water to the same extent.

The effects of dissolved substances, in reducing the freezing points and increasing the boiling points of aqueous solutions, are thus proportional to the concentrations of their molecules. Deviations from this law may take place; they may take place, for instance, in very dilute or concentrated solutions, and various substances in different solvents may exhibit anomalies; but, in general, the principle holds good. Important cases of apparently anomalous behaviour in this respect will be dealt with presently.

The effects of dissolved substances on the freezing and boiling points of solutions are intimately connected with their osmotic pressure. This may be regarded as being due to the diffusing motion of the dissolved particles, just as the pressure exerted by a gas is due to its moving molecules. The extents to which the freezing points are depressed, or the boiling points raised, are in fact measures of this osmotic pressure, and may be regarded as indirect methods of measuring it.

If the space A is filled with a solution of nitrogen

in oxygen and the piston is permeable to oxygen but not to nitrogen, the nitrogen will exert a pressure on the piston. On pushing the piston in, this pressure increases in proportion to the concentration of the nitrogen, since the oxygen passes freely through it. If the space is filled with a solution of sugar in water and the piston is only permeable to the water, the pressure required to force the piston down will be proportional to the concentration of the sugar molecules. This pressure represents the osmotic pressure of the dissolved sugar. Membranes permeable to oxygen and impermeable to nitrogen are not known, but membranes—such as copper ferrocyanide—permeable to water and not to sugar have been utilised. The above experiment is of a theoretical character, but it has been fairly satisfactorily shown, in the case of certain substances, that the osmotic pressure is equal to the pressure that would be exerted were the substance in the state of gas at the temperature and concentration of the solution. The connection between the osmotic pressure and the alteration of the freezing and boiling points can be theoretically deduced, but it here suffices to point out that the connection between the two is indicated by their proportionality to the concentration.

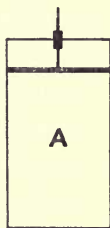


FIG. 5.

§ 7. *Anomalous Behaviour of Common Salt.*—The molecular weight of common salt (NaCl) is 58.45.

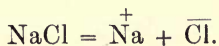
Thus, 58·45 grammes of sodium chloride contain the same number of molecules as 342 grammes of cane-sugar. Now a solution of 58·45 grammes of common salt in 10 litres of water has a freezing point about $0\cdot372^{\circ}\text{C}$. below the freezing point of pure water. Each molecule of salt thus exerts approximately twice the depressing effect on the freezing point of a cane-sugar molecule. In more concentrated solutions, the ratio between the two depressing effects becomes less; but the salt has always a greater influence than its molecular concentration would appear to imply. Similarly, the boiling point of a salt solution is always higher than that of a cane-sugar or glucose solution containing the same number of molecules per unit mass of water. The great majority of salts, alkalies, and acids exhibit the same anomalous behaviour.

This anomaly necessitates an explanatory hypothesis, and this is found in the theory of "electrolytic dissociation".

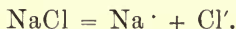
§ 8. *Function and Place of Hypothesis in Science.*—The part played by imagination in science never comes out more clearly than in the framing of hypotheses. The digestion and incorporation within the general scientific system of new and apparently abnormal facts must first be attempted by temporary attempts at explanation. Hypotheses are such temporary explanations. The hypothesis put forth, it must be criticised; and especially it must be tested

by applying it to known phenomena, and by experimental verification of consequences that may be legitimately deduced from it. The value of the hypothesis will be the greater, the more light it sheds upon old facts and the more impetus it gives to successful research. If successful in both or either of these directions, and if not contradicted by observation or experiment, it may fairly claim to rank amongst the working theories of science. The theory of "electrolytic dissociation" has very beautifully and simply rendered more intelligible and consistent a large number of chemical and physical phenomena.

§ 9. *Electrolytic Dissociation.*—This theory explains the abnormal depressing and raising action of dissolved salt on the freezing and boiling points of its aqueous solutions, by supposing that a certain number of salt molecules are dissociated into sodium and chlorine atoms. Since dissolved salt does not liberate hydrogen or oxygen as free sodium and chlorine might be expected to do, and since the solution has neither the colour nor smell of free chlorine, it is further supposed that the sodium and chlorine atoms are charged respectively with positive and negative electricity. Following the nomenclature of Faraday, these positively and negatively charged atoms are known as ions—positive and negative.

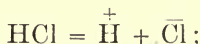


Hence, the term "ionisation" is often applied to such electrolytic dissociation. The same operation is also represented thus :—



By thus cleaving into two ions, some salt molecules do double duty as depressors of the freezing point or raisers of the boiling point of the solution.

Similarly, the various acids, alkalies, and salts that give abnormal results like common salt, are supposed to dissociate electrolytically into ions. Thus hydrochloric acid partially dissociates in the sense :—

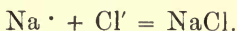
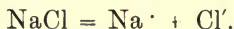


potassium iodide in the sense :—

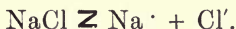


and so on.

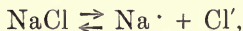
The equation $\text{NaCl} = \text{Na} \cdot + \text{Cl}'$ would appear to imply that all the NaCl molecules cleave into ions. This, however, is not usually the case, since, unless the solution is fairly dilute, the observed depression of the freezing point is not as much as double the theoretical. Moreover, the final ratio between the undissociated molecules and the ions is regarded as being produced and maintained by a balance between the two opposed processes represented thus :—



Neutral molecules continuously cleave into ions, and these ions continuously associate into neutral molecules. The degree of dissociation is determined by a balance between these processes of dissociation and association. It is usual to combine both equations into one by using the sign \rightleftharpoons instead of $=$ thus:—



The sign \rightleftharpoons has also been used—

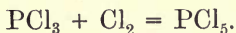


but the former sign is now usually employed.

Cases of dissociation are well known in science. Phosphorus pentachloride, for example, when heated in an enclosed space, partly decomposes into phosphorus trichloride and chlorine.



The extent of this decomposition depends on the temperature and pressure. It increases with rise of temperature, and decreases when the pressure increases. By lowering the temperature sufficiently, the pentachloride may be practically completely regenerated. At any particular temperature and pressure, the three substances PCl_5 , PCl_3 and Cl_2 coexist in virtue of a balance between the simultaneous processes.



These two equations may be combined into the single equation—



This is a typical case of dissociation. The ionisation of common salt is a dissociation process involving the occurrence of electrically charged atoms or ions.

It will be noted that, with respect to the osmotic pressures of solutions, the concentrations concerned are concentrations of particles consisting both of electrically neutral molecules and ions.

§ 10. *Electrolytic Dissociation and Electrolysis.*—It is natural to expect that there should be some connection between the electrolytic dissociation of substances and the general electrical behaviour of their solutions. Substances are known as electrolytes or non-electrolytes according as their solutions conduct or do not conduct electricity. Now sugar is a non-electrolyte and salt is an electrolyte. For all ordinary practical purposes, a sugar solution does not conduct electricity while a salt solution does. This difference in behaviour naturally connects itself with the electrolytic dissociation of the latter. In the same way acids, alkalies, and salts are electrolytes, while substances that are not supposed to be electrolytically dissociated, or ionised, act as non-electrolytes.

This correspondence between the power to conduct electricity and abnormal values for freezing and boiling points is very striking. The conduction of

electricity by an electrolyte is always accompanied by chemical decomposition, and may be regarded in the following way.

Suppose that into a solution of common salt in a glass vessel (A A₁ A₂ A₃) two platinum plates (P and P₁), respectively charged with positive and negative electricity, are introduced. Some of the salt molecules are dissociated into positive and negative ions. These ions will be attracted towards the negative

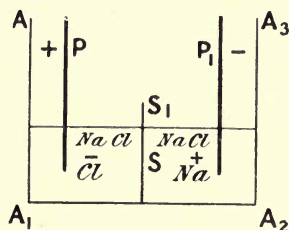
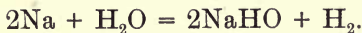


FIG. 6.

and positive plates respectively. The sodium ions will discharge at the negative plate, and the negatively charged chlorine ions at the positive plate. The discharged ions, or atoms, will now act upon the water in the usual way.

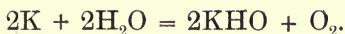
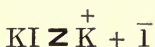


Caustic soda and hydrogen will make their appearance near the negative plate, and hydrochloric acid and oxygen near the positive plate. This is actually

what happens when a current of electricity is passed through the solution in the cell. These effects may be observed by pouring red litmus solution into the solution, and passing an electric current by connecting P and P_1 to a suitable battery. The litmus turns blue near P_1 , and is bleached near P . By using a porous partition, S S_1 , red litmus solution may be introduced round P_1 and blue litmus solution round P . The bleaching effect of the chlorine, however, is apt to obscure the reddening of the blue litmus by the formation of the hydrochloric acid. Gases are evolved in the neighbourhood of P and P_1 at the same time. If these are collected, by allowing them to pass up into tubes containing water and inserted in the liquid, they may be readily shown to consist of hydrogen at P_1 and oxygen at P .

Electrolytic dissociation is thus brought into connection with the phenomenon of electrolysis in an electrolytic cell. P and P_1 are the electrodes— P_1 being distinguished as the cathode and P as the anode. The current is conventionally spoken of as passing from anode to cathode. The ions Na^+ and Cl^- are termed respectively cations and anions—cations because they seek the cathode, and anions because they travel to the anode.

If a solution of potassium iodide is electrolysed in the same way, a brown stain of iodine appears at the anode, and caustic potash and hydrogen make their appearance at the cathode.



Further reactions may take place when the chlorine or iodine liberated at the anode comes in contact with the alkali diffusing from the cathode, but the above reactions are the first to take place.

The liberation of the ion at the electrode—iodine at the anode—is usually spoken of as a primary action. Secondary actions result from interaction between the liberated ions and the solution (or the electrode). The action of the sodium on the water is such a secondary action.

The passage of a current of electricity through an electrolytic cell may thus be regarded as a carriage of charges of positive and negative electricity in opposite directions through the liquid to the two electrodes by the cations and anions.

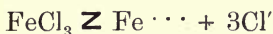
§ 11. *Faraday's Law*.—Suppose that during the electrolysis of common salt one of the cations discharges at the cathode. The solution now contains an excess charge of negative electricity, borne by the anion corresponding to the discharged cation. This will tend to prevent the discharge of other cations, until the excess of negative electricity is got rid of by the discharge of the extra anion. This implies that as many cations discharge during a certain time as anions. Similar remarks apply to the electrolysis of

other solutions—such as potassium iodide. Equivalent quantities of iodine and potassium would thus be expected to appear at anode and cathode during a certain time. Since the potassium produces its equivalent of hydrogen, the amounts of iodine and hydrogen produced in a certain time during electrolysis may fairly be expected to be equivalent. Moreover, the greater the current, the more rapidly will the ions discharge, and the greater will be the actual amounts of caustic potash and iodine produced in a second of time. Since the current strength is simply the quantity of electricity passing through the cell in unit time, this means that the passage through the cell of any definite quantity of electricity results in the production at the electrodes of chemically equivalent quantities. This is equivalent to the statement that the hydrogen produced at the cathode by a unit of electricity—the electro-chemical equivalent of hydrogen—is chemically equivalent to the iodine produced at the anode—electro-chemical equivalent of iodine. Faraday showed that the products of electrolysis are so chemically equivalent.

If a current of electricity is passed through two electrolytic cells arranged in series, one containing silver nitrate solution and the other a solution of common salt, silver is deposited at the cathode of the former, and caustic soda and hydrogen make their appearance at the cathode of the latter. The quantity of electricity passing through each cell in unit

time is the same, and the silver, hydrogen, and caustic soda are formed in equivalent amounts.

In the case of a substance like ferric chloride (FeCl_3), the equivalent of the iron is its atomic weight divided by its valency (three). Iron is deposited during the electrolysis of its trichloride in the proportion of this equivalency. This may be explained by assuming the electrolytic dissociation

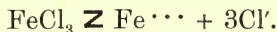
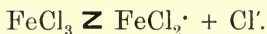


to take place.

Each valency is represented by a definite, constant charge of positive or negative electricity. It is then evident that the discharge of $1\text{Fe} \cdots$ must be accompanied by the discharge of $3\text{Cl}'$ —since every positive charge leaving the solution means a corresponding loss of one negative charge. Similar remarks apply to other molecules containing atoms of higher valency than one.

§ 12. *Condition of Dissolved Electrolytes.*—When a salt is dissolved in water, the electrolytic dissociation or ionisation theory supposes that a certain number of its molecules cleave into ions. The original molecules are electrically neutral, and the negative and positive charges on the anions and cations are equivalent. Thus the positive charges on the sodium ions and the negative charges on the chlorine ions, when sodium chloride is dissolved in water, are equal to one another. Similarly, with regard to the ferric and chlorine ions, when iron per-

chloride is dissolved in water. Dissociation may take place in the latter case according to the equations—



A valency, as it were, is represented in the resulting ions by a definite, constant quantity of positive or negative electricity.

The undissociated molecules and dissociated ions are regarded as continuously dissociating and recombining, as they move in the solution. At definite concentrations, there are always definite proportions of dissociated and undissociated molecules. This is indicated by the constant freezing and boiling points of these solutions. The ratio of undissociated to dissociated molecules differs with different substances and to a certain extent differs with the concentration, but it is definite for any substance at a particular concentration in pure water at a definite temperature.

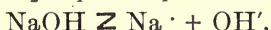
Currents of electricity pass through these solutions by the haphazard movements of the ions giving place to steady streamings of anions and cations to their respective electrodes. Their behaviours at these electrodes produce the characteristic chemical changes occurring in electrolysis.

Acids and alkalies are similarly electrolytically dissociated into ions. The abnormal depression of the freezing point, and the evolution of hydrogen

and chlorine at the cathode and anode during electrolysis of a solution of hydrochloric acid gas in water, are explained by the dissociation



Similar dissociations are represented by such equations as—



§ 13. *Conductivity and Electrolytic Dissociation.*

—A piece of copper wire offers less resistance to the passage of an electric current than an iron wire of similar dimensions. The conductivity—or power to conduct—of the copper is therefore evidently greater than that of the iron. Conductivity and resistance are reciprocals, and the less the latter is, the greater is the former. In the same way, different solutions have different conductivities.

According to the electrolytic dissociation theory, the conductivity of any solution depends upon the ions it contains. The passage of the electric current, for example, through a solution of common salt, is connected with the streaming of the chlorine anions and the sodium cations to their respective electrodes. The greater the number of these ions, the more readily will the current pass—the greater is the conductivity of the solution. The speeds of the ions also affect the conductivity—the greater the sum of

the speeds of the cations and anions, the greater the conductivity.

It is convenient to consider the molecular or equivalent conductivities of such solutions. The molecular conductivity is the conductivity of a solution containing 1 gramme molecule of the substance. The equivalent conductivity is the conductivity of a solution containing 1 gramme equivalent of the substance. Thus, the conductivity of 1 litre of normal sulphuric acid (containing 49 grammes acid to the litre) is the equivalent conductivity of sulphuric acid at that dilution, and the conductivity of 2 litres of sulphuric acid (containing 24.5 grammes of acid per litre) is the equivalent conductivity of sulphuric acid at that dilution. In all cases, the particular volume of the solution containing the gramme equivalent is supposed to be contained between two electrodes 1 centimetre apart.

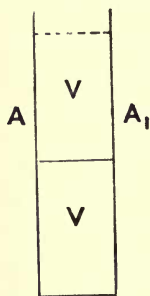


FIG. 7.

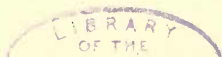
It is also convenient to embody the results of the measurements on equivalent or molecular conductivities in one experiment of a somewhat theoretical nature.

A solution of salt, containing 58.45 grammes (its gramme-molecular weight) in volume \bar{V} , is placed in a vessel between two platinum electrodes, A A₁, 1 centimetre apart. The conductivity of this is the molecular conductivity. One diluting to $2\bar{V}$, the molecular

conductivity is found to increase. Neglecting the sum of the speeds of the ions, which remains practically constant, the increase in conductivity is evidently due to an increase in the number of ions. If the conductivity were simply due to the salt molecules, irrespective of any dissociation, there is no reason why dilution should increase the conductivity, since at all dilutions the same number of molecules is available.

The molecular conductivity increases with the dilution, until at great dilution it attains a maximum. This represents complete dissociation of the salt into Na^+ and Cl^- ions—or at any rate as complete a dissociation as can be obtained. By comparing the conductivities at various stages of dilution with this maximum conductivity, the dissociations corresponding to these stages of dilution can be estimated. Thus, let $\lambda \bar{V}$ be the molecular conductivity when 1 gramme molecule is contained in volume \bar{V} of the solution, and $\lambda \infty$ be the maximum molecular conductivity. Also let X represent the degree of dissociation—equalling 1 when the dissociation is complete and 0 when no molecules are dissociated—and $U + V$ equal the sum of the speeds of the ions. Then, since the molecular conductivities are proportional to the sum of the ion speeds and to the number of dissociated molecules

$$\lambda \bar{V} = K \cdot X \cdot (U + V) \text{ and } \lambda \infty = K \cdot (U + V)$$



($X = 1$ at infinite dilution). Thus

$$\frac{K \cdot X \cdot (U + V)}{K(U + V)} = \frac{\lambda \bar{V}}{\lambda \infty} \text{ or } X = \frac{\lambda \bar{V}}{\lambda \infty}.$$

Thus, the degrees of dissociation of various substances at different dilutions may be determined.

§ 14. *Degree of Electrolytic Dissociation and the Freezing Points of Solutions.*—The extent to which a dissolved salt depresses the freezing point affords a measure of its electrolytic dissociation. If a solution of 58.45 grammes of common salt in 1 litre of water were entirely undissociated, it would have the same freezing point as a solution of 342 grammes of cane-sugar in the same mass of water. If every sodium chloride molecule were dissociated, the depression would be double that produced by the sugar. By determining the actual depression, the ratio of undissociated to dissociated molecules can be determined. For if D' be the actual depression found, and D the depression on the assumption that no molecules are dissociated; and if X , as before, is the ratio of dissociated to undissociated molecules, then—

$$D' = D(1 + X).$$

In a similar way, determinations of the boiling points of solutions may be used to determine X . In the case of molecules dissociating into N ions the formula would be—

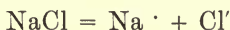
$$D' = D \times (1 + \overline{n - 1 x}).$$

§ 15. *Parallelism between Conductivity and Freezing Point Methods.*—Now, determination of X by conductivity and freezing point (or boiling point) methods confirm one another. Both methods indicate that the degree of electrolytic dissociation increases with the decrease of concentration of the solution; and the actual extents of dissociation, as determined by either method, agree well within the limits of experimental error. This parallelism justifies the application of the theory to the general behaviour of dissolved electrolytes. The value of this theory will be most fully realised by considering a number of ordinary chemical reactions taking place in solution, either with or without electrolysis. It is the object of the following chapters to show that the application of the ionisation theory to many chemical reactions helps considerably to elucidate a large number of chemical phenomena.

CHAPTER II.

IONS AND PRECIPITATION.

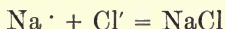
§ 16. *Relation between Dissolved Molecules and Ions.*—A solution in water of common salt is supposed to contain undissociated molecules of NaCl, Na⁺, and Cl⁻ ions. The molecules and ions are in constant motion; and NaCl molecules are constantly dissociating into ions, and the ions recombining into electrically neutral molecules. At definite concentration, there is always, on balance, a definite ratio between dissociated and undissociated molecules. It is evident that, the greater the concentration of the NaCl molecules, the greater number of these will cleave into ions in any given time. The tendency for the dissociation



to take place will therefore be proportional to C, where C is the concentration of the NaCl molecules. The concentration C is expressed in gramme-molecular weights of the salt per unit mass of solvent (whatever may be fixed on). Thus, C would be the same for 58.45 grammes of NaCl molecules per 1,000 grammes of water as for 74.51 grammes of KCl per

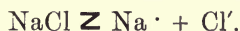
1,000 grammes of water. The concentration is thus referred to the molecules.

Similarly, the tendency for the association



to take place is proportional to the concentrations of the $\text{Na} \cdot$ and Cl' ions. For the more $\text{Na} \cdot$ ions there are in volume V of the liquid, the more often will some of them come within the sphere of influence of the Cl' ions. A similar statement applies to the Cl' ions. If, then, C_1 and C_2 are the concentrations of the $\text{Na} \cdot$ and Cl' ions, the tendency to associate will be proportional to the product $C_1 \times C_2$.

The dissociation and association equations may be combined by writing the single equation—



Where the sign \rightleftharpoons indicates that changes from right to left and left to right proceed simultaneously. The sign \rightleftharpoons has been used instead of the sign \rightleftharpoons . The rate of change from left to right = $K_1 C$, and the rate of change from right to left = $K_2 (C_1 \times C_2)$, if K_1 and K_2 are constants. Thus $K_1 C = K_2 (C_1 \times C_2)$

or $KC = C_1 \times C_2$ where $K = \frac{K_1}{K_2}$. This is a simple

case of mass-action. K is the dissociation constant, and is evidently connected with the quantity X of paragraph 13. Since $C_1 = C_2$ the equation may also be written $KC = C_1^2 = C_2^2$. As will be seen in the next paragraph, the form $KC = C_1 \times C_2$ is usually to be

preferred, since the values of C_1 and C_2 may be altered in different degrees by the presence of other substances in the solution.

It must be carefully observed that the concentrations refer to the gramme-molecular weight concentrations—to the concentrations of the particles as distinct from their actual masses. Thus, 35.45 grammes of chlorine ions in 1,000 grammes of water, and 23 grammes of sodium ions in 1,000 grammes of water, are equal concentrations.

A consideration of the equilibrium equation $KC = C_1 \times C_2$ indicates clearly why the ionisation of a salt solution increases with dilution. For, suppose that in volume V there are 4 molecules, and that 2 of these are dissociated. Then $C = C_1 = C_2 = 2$ and $K = 2$. If the solution is now diluted until 2 molecules are contained in volume V , and if, as before, half the molecules are dissociated, then $C = C_1 = C_2 = 1$. But 2×1 does not equal 1×1 , and since K is a constant, it is evident that the ratio of dissociated to undissociated molecules must increase. Similar considerations, of course, apply to other solutions of electrolytes.

The values assigned above to K , etc., are purely theoretical values, and are only used to bring out the general principle. It is obvious, from the above considerations, that in very dilute solution the dissociation is practically complete. A theoretical interpretation of the rise in molecular conductivity

with increasing dilution, until a maximum is obtained at a high degree of dilution, is thus afforded.

§ 17. *Precipitation of Salt by Hydrochloric Acid.*—When water stands in contact with more than enough salt to saturate it, salt passes from the solid to the dissolved state and *vice versâ*. When the two processes finally balance one another, the salt solution is saturated. There is then equilibrium between the solid undissolved salt and the undissociated molecules of NaCl. There is also equilibrium between the undissociated salt molecules and the ions. As seen in the last paragraph this equilibrium may be represented by $\frac{C_1 \times C_2}{C} = K$.

Evidently an increase in C_2 would necessitate an increase in C —the concentration of the NaCl molecules. Since the solution is saturated with respect to these, this would mean a deposition of salt. This increase in C_2 —the concentration of the Cl' ions—can be produced by saturating the solution with hydrochloric acid gas. The dissociation



puts more Cl' ions into the solution, and C_2 is increased. As is well known, salt is deposited from concentrated brine when hydrochloric acid gas is led into the solution. The greater insolubility of common salt in hydrochloric acid solution than in water thus finds a ready explanation.

Concentrated hydrochloric acid will precipitate barium chloride from its aqueous solution in a similar way. The dissociation of the barium chloride takes place in two stages thus:—



Taking the total dissociation



for the sake of simplicity, we have as usual

$$\frac{C_1 \times C_2 \times C_2}{C} = K \text{ or } \frac{C_1 \times C_2^2}{C} = K$$

where C , C_1 and C_2 represent the concentrations of the barium chloride, barium ions, and chlorine ions respectively. The C_2^2 occurs in the equation because two chlorine ions correspond to one barium ion. As in the case of the salt, the introduction of chlorine ions by the dissociation of the hydrochloric acid necessitates an increase in C —the concentration of the barium chloride molecules. As soon as the saturation point for these is passed they are precipitated.

It has been shown that when the quantity $C_1 \times C_2$ or $C_1 \times C_2^2$ exceeds a certain value some of the salt is precipitated. This value has been termed the solubility-product. It represents the product of the concentrations of the ions when the solution is saturated with respect to the solute.

§ 18. *Precipitation Reactions Due to Ions.*—Solutions of sodium chloride and potassium chloride

both give precipitates of silver chloride with silver nitrate. A little chloroform gives no precipitate when shaken up with the silver solution. Since chloroform (CHCl_3) is a non-electrolyte, and the chlorides of sodium and potassium are electrolytes, it is natural to refer the behaviour of the two latter to their Cl' ions. The silver nitrate solution contains AgNO_3 , $\text{Ag} \cdot$ and NO_3' , while the alkali chloride solution contains RCl , $\text{R} \cdot$ and Cl' ($\text{R} = \text{K}$ or Na). The Cl' and $\text{Ag} \cdot$ combine to form AgCl , which falls as the well-known precipitate.

In a similar way, the various precipitations employed in analytical chemistry can be referred to the presence of ions. All solutions of sulphates contain SO_4'' , and therefore all give precipitates of barium sulphate when $\text{Ba} \cdot \cdot$ ions are added by means of a barium chloride or barium nitrate solution. Cadmium salts all give the usual reactions for cadmium, because they one and all contain $\text{Cd} \cdot \cdot$ ions. Soluble ferrous salts give the same precipitates with alkalies, sulphuretted hydrogen and potassium ferricyanide, because they all contain $\text{Fe} \cdot \cdot$ ions; and the reactions of all ferric salts are the same with such reagents as ammonia, because they all contain $\text{Fe} \cdot \cdot \cdot$ ions when in solution.

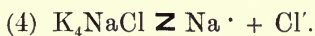
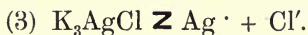
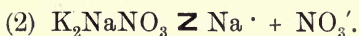
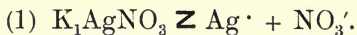
As is often the case, an apparent exception here helps to emphasise the rule. Mercuric salts give a characteristic precipitate with potassium iodide. This precipitate is yellow, rapidly changing to red, and is

soluble in excess of the precipitant. This precipitate of HgI_2 is formed by the combination of $\text{Hg} \cdot \cdot$ and $2\text{I}'$ ions. It would, therefore, be expected that whenever $\text{Hg} \cdot \cdot$ and I' ions are brought together, precipitation of HgI_2 will occur. A solution of mercuric cyanide gives no precipitate with potassium iodide. This anomalous behaviour, however, confirms the contention that the mercuric iodide results from combination between $\text{Hg} \cdot \cdot$ and $2\text{I}'$ ions, because mercuric cyanide has been found not to dissociate to any extent into $\text{Hg} \cdot \cdot$ ions.

Some precipitations are much more complete than others. Lead sulphate, for example, is less completely precipitated from lead solutions by a soluble sulphate than is barium sulphate from barium solutions. Silver chloride is more completely precipitated by sodium chloride than is lead chloride. The solubility of the precipitates in water, of course, has much to do with this. Precipitation can often be made more complete by adding liquids to the water in which the precipitate is less soluble. The addition of alcohol, for instance, renders the precipitation of lead sulphate more complete. A familiar analytical device for securing complete precipitation, or as complete a precipitation as possible, is to add excess of the precipitant. Silver is only completely precipitated from silver nitrate solution by the addition of rather more than the equivalent quantity of sodium chloride. Silver chloride is rather more insoluble in a dilute

sodium chloride solution than in pure water or sodium nitrate solution. From the "ionisation" point of view this can be readily explained. The mixed solutions of silver nitrate and sodium chloride contain AgNO_3 , NaCl , $\text{Ag} \cdot$, $\text{Na} \cdot$, NO_3' , Cl' , NaNO_3 and AgCl . Let the symbols represent the concentrations of these molecules and ions. Silver chloride is slightly soluble in water—indeed it seems probable that no salt is absolutely insoluble.

This solubility of silver chloride in water can be shown to exist by determinations of the electrical conductivity of its solution. The solution of silver chloride has a greater conductivity than pure water, and determinations of the actual conductivity can be employed to indicate the extent of the solubility. The final equilibrium can be represented by the equations—



The solution, however, contains very few $\text{Ag} \cdot$ ions, since the great insolubility of the silver chloride removes most of them. $\text{Ag} \cdot$ and Cl' ions unite to form silver chloride, and this, when formed, precipitates and no longer takes part in maintaining the equilibrium in solution. A small amount, however, of silver chloride remains in solution, which is satu-

rated with respect to it. Obviously, an excess of sodium chloride results in an accumulation of Cl' ions, and the concentration of these, according to (3), results in a further formation of silver chloride which at once precipitates. The sodium chloride thus acts towards the silver chloride as hydrochloric acid acts towards the salt itself. It would also appear from the equations, that it might be possible to cause a further precipitation of silver chloride by increasing the concentration of the $\text{Ag} \cdot$ ions—that is, by adding silver nitrate. This might be expected to take place when there has not been sufficient addition of common salt to prevent an appreciable amount of $\text{Ag} \cdot$ ions being present in the solution. It has been experimentally shown, that in solutions containing certain relative amounts of silver nitrate and sodium chloride, the addition of either silver nitrate or sodium chloride will produce a further precipitate of silver chloride. This fact affords a very beautiful illustration of the value of the “ionisation” idea.

The amount of silver chloride that can exist in the solution is determined by the solubility-product $\text{Ag} \cdot \times \text{Cl}'$. When further Cl' or $\text{Ag} \cdot$ ions are added, AgCl is formed, until the value of $\text{Ag} \cdot \times \text{Cl}'$ again reaches the solubility-product. The AgCl so formed is precipitated, since the solution is saturated with respect to it. Excess of silver nitrate must therefore be added when it is used for precipitating chlorine from a salt solution, and excess of sodium chloride

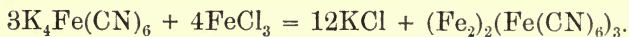
must be employed to precipitate silver completely from its solution.

Similar remarks apply to other precipitations. It is evident that the more soluble a precipitate is, the greater does its solubility-product tend to be, and the more difficult does it become to completely precipitate it. The magnitude of the solubility-product also depends on the extent of dissociation, and this tends to further complicate matters. In the case of very dilute solutions, complete dissociation practically takes place. A substance like silver chloride, which is exceedingly slightly soluble in water, may therefore be regarded as completely dissociated. Thus the solubility-products of very slightly soluble precipitates are practically determined by their solubility.

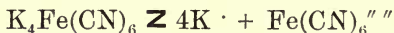
§ 19. *Ions and Constitution.*—If the reactions between salts, acids, bases, etc., take place between the ions, the constitution of the precipitates formed should give information with regard to the nature of the reacting ions. Silver nitrate solution gives a white precipitate of silver chloride with a solution of sodium chloride. The formation of the precipitate AgCl indicates the existence of Cl' (and $\text{Ag}\cdot$) ions. A solution of potassium platinichloride (K_2PtCl_6) gives with silver nitrate a yellow precipitate. The composition of this precipitate is Ag_2PtCl_6 . This indicates that the ions of potassium platinichloride are $2\text{K}\cdot$ and PtCl_6'' . The behaviour of salts under electrolysis affords confirmation of the natures of

their ions. In the electrolysis of potassium platini-chloride, the potassium is found to travel to the cathode and the platinum and chlorine to the anode. This is precisely what $K \cdot$ and $PtCl_6''$ ions would be expected to do.

The failure of ammonia solution to produce a precipitate in a solution of potassium ferrocyanide ($K_4Fe(CN)_6$) indicates that the iron does not exist in the form of ions. Curiously enough, a solution of this salt gives precipitates with solutions containing iron ions. The reaction with ferric chloride takes place according to the equation—



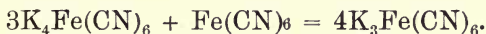
This indicates that the ionisation of potassium ferrocyanide takes place thus:—



a supposition confirmed by electrolysis.

When a solution of potassium ferrocyanide is electrolysed, the liquid round the cathode becomes alkaline, and at the anode there may appear potassium ferricyanide, oxygen, prussic acid or Prussian blue ($(Fe_2)_2(Fe(CN)_6)_3$). The production of these substances is readily explicable by the ionisation of potassium ferrocyanide into $K \cdot$ and $Fe(CN)_6'''$ ions — $K_4Fe(CN)_6 \rightleftharpoons 4K \cdot + Fe(CN)_6'''$. The potassium ions travel to the cathode and there produce caustic potash and hydrogen as usual. The fate of the anions depends upon circumstances. If there is sufficient

concentration of the potassium ferrocyanide at the anode, potassium ferricyanide may be produced according to the equation—



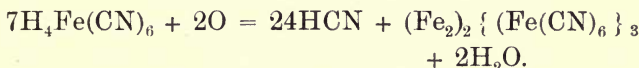
In the case of more dilute solutions—and especially if the solution is slightly acidified with prussic acid—hydroferrocyanic acid may be produced by interaction between water and the $\text{Fe}(\text{CN})_6$. The equation



is analagous to the action



Prussian blue may then be produced by the oxidation of the hydroferrocyanic acid by the electrolytic oxygen :—

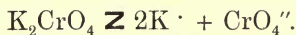


Potassium cyanide gives with silver nitrate solutions a white precipitate of silver cyanide. This silver cyanide dissolves in excess of the precipitant, and a solution of the double cyanide of silver and potassium is formed. This double salt has the composition $\text{KAg}(\text{CN})_2$. Since the addition of caustic soda produces no precipitate in the solution, Ag^+ is probably not one of the ions. On electrolysing the solution, therefore, the silver might be expected to travel to the anode as the anion $\text{Ag}(\text{CN})_2^-$. This is actually the case—the anode being covered with a

deposit of silver during the electrolysis. Silver, however, is also deposited at the cathode—this has been shown to be due to the decomposition of the solution by the discharged K^{\cdot} ions. The deposition of the silver at both electrodes cannot be due to a halving of the metal between the cations and anions, because each deposition is equivalent to the amount of electricity passing through the electrolytic cell. This can only be explained by equivalents of silver and potassium appearing at the anode and cathode respectively, and the secondary production of an equivalent of silver by the potassium.

In a similar way the double iodide of potassium and mercury, formed by dissolving mercuric iodide in potassium iodide ($KHgI_4$), gives no precipitate with caustic soda and therefore contains no $Hg^{..}$ ions. Nessler's solution for the detection and estimation of small quantities of ammonia, consists of a solution containing the double iodide of mercury and potassium and caustic potash. This solution gives a yellow colour, or precipitate, with water containing ammonia.

The chromium in a solution of potassium chromate is not precipitated by alkalies, because chromium ions are not present in the solution. The ionisation of potassium chromate is indicated by its behaviour under electrolysis, and proceeds according to the equation—



When potassium chromate solution is electrolysed in an electrolytic cell, with a porous diaphragm between the anode and cathode compartments, caustic potash and hydrogen form in the latter, and oxygen and potassium bichromate in the former. The caustic potash and hydrogen are, as usual, formed by the liberated potassium, while the increase of chromium content, indicated by the change of chromate into bichromate, is evidently connected with the passage of CrO_4^{--} anions into the anode compartment. The production of a precipitate of red silver chromate (Ag_2CrO_4), when silver nitrate solution is added to potassium chromate solution, indicates the existence of CrO_4^{--} ions in the latter.

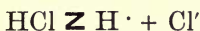
In these and in many other reactions, the parallelism between the behaviour of dissolved substances towards chemical reagents and their decompositions under electrolysis, finds ready expression in terms of their ionisation.

CHAPTER III.

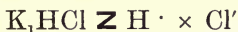
THE HYDROGEN AND HYDROXYL IONS.

§ 20. *Acids, Alkalies and the Hydrogen and Hydroxyl Ions.*—Soluble chlorides have the common property of precipitating silver chloride from silver solutions, because they have the common ion Cl' . Acids are dissociated electrolytically in solution, as indicated by their being electrolytes and by their abnormally depressing the freezing point. Their common properties must therefore be referred to their common ion. The acidity of hydrogen chloride indicates that this common ion is that of hydrogen. The chlorine ion certainly does not confer acid properties on its solution, and there only remains the hydrogen ion. All acids are known to contain hydrogen, and an investigation of the reactions into which they enter, confirms the belief that they are characterised by their hydrogen ions when in solution. This confirmation is the more complete, inasmuch as not only can the reactions of acids be shown to be connected with the presence of hydrogen ions, but their strengths are found to be proportional to the extent of their dissociation.

For instance, hydrochloric and acetic acids are dissociated according to the equations—



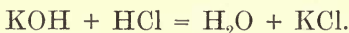
Acetic acid is undoubtedly a weaker acid than hydrochloric acid. Hydrochloric acid will prevent the precipitation of calcium oxalate, for example, while acetic acid will not. The two equilibrium equations can, as usual, be represented by—



when the symbols HCl, etc., represent the respective concentrations. Conductivity experiments show that K_1 is greater than K_2 . This means that the concentration of the hydrogen ions is greater in a solution of hydrochloric acid than in a solution of acetic acid of the same concentration—unless the solutions are very dilute. The greater strength of the hydrochloric acid is therefore referable to its greater ionisation. Similarly, the very slight ionisation of carbonic acid is connected with its weak acid properties.

In the electrolysis of acids, hydrogen appears at the cathode, just as the various metals appear there during the electrolysis of their salts. This corresponds with the idea of an acid as a “salt of hydrogen”—the sour taste and colour reactions with litmus, etc., being due to the hydrogen ions. Acids in general react with alkalies to form salts and water. Caustic

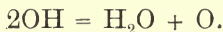
potash and hydrochloric acids, for example, react to produce water and potassium chloride.



Caustic potash in solution is ionised into potassium and hydroxyl ions.



During the electrolysis of such a solution the potassium ions visit the cathode, and there regenerate caustic potash with the liberation of hydrogen. The hydroxyl ions travel to the anode, where they discharge and decompose into water and oxygen.



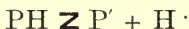
The final result thus being the decomposition of the water into hydrogen and oxygen, while the amount of caustic potash (though not its concentration) remains unchanged. The reaction between the caustic potash and hydrochloric acid is readily explained by the union of the hydroxyl and hydrogen ions to form water. The heat evolved during the reaction must be ascribed mainly to this. This is proved by the experimental fact that the heats of reaction between dilute solutions containing equivalent amounts of strong acids and strong caustic alkalies are the same. Thus the same amount of heat is given out when 49 grammes of sulphuric acid act upon 56 grammes of caustic potash in dilute solution, as when 36.45 grammes of hydrochloric

acid act upon 40 grammes of caustic soda in dilute solution. Experiments on the conductivity of water show that it is very slightly dissociated. Equivalent quantities of acids and alkalies contain corresponding numbers of H^+ ions and OH^- ions. Since, in dilute solutions, the acids and alkalies are practically completely dissociated into H^+ and OH^- , these practically all combine to form undissociated H_2O molecules. In this way, the above equality of neutralisation heats is readily explained.

The characteristic production of hydroxides of the heavy metals, when caustic soda or potash solutions are added to solutions of their salts, indicates the presence of hydroxyl ions in the solutions of caustic alkalies. The production of cupric hydrate ($Cu(OH)_2$), by the addition of sodium hydrate to copper sulphate solution, is an indication of the presence of OH^- ions in the solution of the caustic soda. When oxides are precipitated by caustic soda, as from mercuric chloride solution, these may be regarded as produced by the decomposition of the initially formed hydrates ($Hg(OH)_2 = HgO + H_2O$).

§ 21. *Theory of Indicators.*—An acid reaction to litmus, methyl orange, etc., is connected with the presence of hydrogen ions, an alkaline reaction with the presence of hydroxyl ions. The actions of the hydrogen and hydroxyl ions on indicators can be interpreted by supposing that the indicators themselves are weak acids or bases.

Phenolphthalein is colourless in the presence of acid and is reddened by alkalies. It may be represented as PH , where P represents the complex anion and H the cation. In solution it is slightly dissociated in the sense—



If C , C_1 and C_2 represent the concentrations of the undissociated molecules, the anions and the cations respectively, the equilibrium between these may be represented as usual by the equation—

$$K = \frac{C_1 \times C_2}{C}$$

Since K is very small, by hypothesis, the solution mainly contains undissociated molecules, and these are evidently colourless. On adding caustic soda to the solution, hydroxyl ions are introduced, and some of these combine with the hydrogen ions to form water. This process diminishes C_2 , and a further dissociation of the PH molecules takes place to meet the demands of the equation. The red colour is evidently due to the P' ions. On adding hydrochloric acid to the alkalinised indicator, the hydrogen ions remove the excess of hydroxyl ions to form water, and if added in sufficient quantity increase the value of C_2 . Colourless PH molecules then form and the red colour disappears.

Methyl orange is an acid indicator that reddens with acids and turns yellow in alkaline solution.

These colour changes may be explained by assuming that it dissociates according to the equation—



where M' is yellow and MH is red.

It is evident that the more strongly the indicator dissociates, the less sensitive it will be to acids. The more strongly it dissociates, the greater the concentration of the hydrogen ions in its solution. The addition of hydrogen ions will evidently have less effect on a greater original concentration than on a smaller.

For, suppose that a solution of an indicator A has a concentration C and that it is so dissociated as to introduce into volume V of the solution one hydrogen ion. The concentration of its hydrogen ions may then be represented as one. Suppose, further, that a solution of an indicator B has also concentration C , but introduces two hydrogen ions into volume V of its solution. The concentration of its hydrogen ions may be represented as two. On adding to the solutions of the two indicators enough acid to introduce one extra hydrogen ion into volume V , it is evident that whereas (neglecting any slight increase in volume due to the addition of the acid) in the case of A the concentration of the hydrogen ions is doubled, in the case of B their concentration is only increased in the proportion of three to two. Obviously, the acid will have more effect on A than on B.

This being so, methyl orange must be more dissociated than phenolphthalein, because while the latter is appreciably affected by carbonic acid methyl orange is not. This can readily be shown by passing carbon dioxide through slightly alkalised solutions of the two indicators.

The greater dissociation of methyl orange, however, makes it more sensitive to alkalies than phenolphthalein. This follows from the fact that the alkali acts by completely (or almost completely) removing the hydrogen ions. The more hydrogen ions there are to remove, the greater will be the effect of the alkali. If an alcoholic solution of strychnine be poured into faintly acidified solutions of phenolphthalein and methyl orange it will only alter the colour of the latter.

It should be added that commercial methyl orange is usually the sodium salt. Slight acidification will then introduce some of the free acid into the solution.

Of course, the value of the methyl orange as an indicator also depends upon the fact that it does not dissociate to too great an extent—or else it would always be yellow, except in the presence of a considerable excess of hydrogen ions, and perhaps not even then.

Thus methyl orange is the better indicator of the two to use for the titration of bases, and phenolphthalein for the titration of acids.

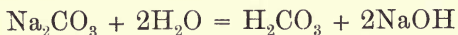
The greater sensitiveness of phenolphthalein to

carbonic acid makes it more unsuitable than methyl orange for use as an indicator during the titration of carbonates. The carbonic acid produced during the reaction affects the result by affecting the phenolphthalein, while methyl orange gives practically the correct end-point in virtue of its comparative indifference towards the carbon dioxide.

Similar considerations apply to basic indicators. In the case of these, the more strongly ionised are more sensitive to acids and less sensitive to alkalies.

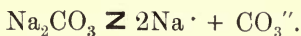
It ought, perhaps, to be added that the older theory of indicators makes the suggestion that the characteristic colour changes take place according as the indicator exists free, or as a salt. It will be noted that in speaking of acid, alkaline or neutral reactions, the terms should be used with respect to definite indicators. When no indicator is mentioned, it is understood that the term is applicable to any indicator.

§ 22. *Alkalies and Hydroxyl Ions.*—The ionisation hypothesis readily suffices to explain the alkaline reaction of a salt like sodium carbonate, by showing that its solution must contain hydroxyl ions. Without the aid of this hypothesis the alkaline reaction of sodium carbonate solution would be explained by a partial decomposition in the sense—

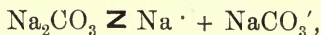


the strong alkali being supposed to overcome the

weak acid. The sodium carbonate is ionised, when in solution, according to the equation—

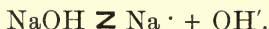


For the sake of simplicity the first stage of the dissociation, *viz.*,

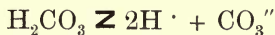


is omitted.

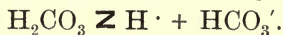
In the solution there are a certain number of hydrogen and hydroxyl ions in equilibrium with the undissociated water molecules. The introduction of sodium ions means that an equilibrium between sodium ions, hydroxyl ions and undissociated caustic soda molecules must be established.



Caustic soda is a strong base and is strongly dissociated. A considerable number of hydroxyl ions must therefore make their appearance to maintain the equilibrium. The hydrogen ions necessarily produced at the same time must be in equilibrium not only with the hydroxyl ions and undissociated water molecules, but also with the CO_3'' ions and the undissociated molecules of H_2CO_3 .



and



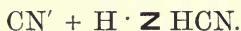
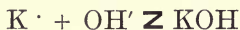
But since carbonic acid is a weak acid and does not dissociate to any great extent, a much greater number of hydrogen ions will combine to form carbonic acid than hydroxyl ions to form caustic soda.

An excess of hydroxyl ions thus remains to impart an alkaline character to the solution.

A similar explanation applies to the alkaline reaction of a solution of potassium cyanide. Dissociation takes place into potassium and cyanogen ions.



The hydroxyl and hydrogen ions resulting from the dissociation of the water molecules must then be in equilibrium with these ions according to the equations—



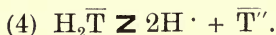
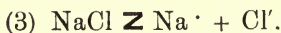
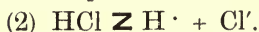
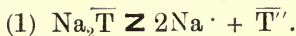
Caustic potash, being a strong base, demands the presence of a considerable number of hydroxyl ions, while the weakness of the prussic acid results in most of the dissociated hydrogen ions combining with the cyanogen to form hydrogen cyanide molecules. The perceptible smell of prussic acid in a potassium cyanide solution shows that it is really produced.

Similar considerations apply to the alkaline reactions of salts like borax, where a strong base is combined with a weak acid.

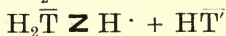
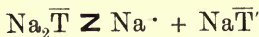
§ 23. *Weakening of Acid Strengths.*—The acid and alkaline strengths of solutions depend on the concentrations of their hydrogen or hydroxyl ions. The actions of acids on indicators or in effecting the solution of precipitates may therefore be interfered with by diminishing the concentrations of their hydro-

gen ions. The addition of the salt, particularly the sodium or potassium salt, of a weak acid will diminish the concentration of the hydrogen ions of a strong one. This is due to the withdrawal of hydrogen ions from the solution by the anions produced during the dissociation of these salts. As a rule, the sodium and potassium salts of acids are more strongly dissociated than the acids themselves. By the ionisation of the sodium or potassium salt of a weak acid there is therefore produced in the solution a comparatively great concentration of the anions of the weak acid. These anions combine with some of the hydrogen ions afforded by the dissociation of the strong acid, and thus produce a weakening of acid strength.

If a solution of sodium tartrate is added to hydrochloric acid it weakens the acid strength of the latter very considerably. The solution contains undissociated molecules and ions in equilibrium with one another as indicated by the following equations—



The two dissociations

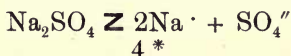


are omitted for the sake of simplicity.

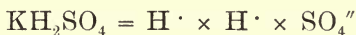
Some of the \bar{T}'' ions provided by the dissociation of the sodium tartrate combine with hydrogen ions to form tartaric acid molecules. Further dissociations of the sodium tartrate and hydrochloric acid may help to restore the balance. These further dissociations are, however, limited by the general conditions of the equilibrium. Tartaric acid is a much weaker acid than hydrogen chloride, and dissociates much less strongly than the strong hydrochloric acid. It also ionises to a less extent than its sodium salt. The final result is, therefore, a considerable withdrawal of hydrogen ions from the solution and a corresponding diminution in acid strength.

This diminution of acidity can easily be verified by adding a solution of sodium tartrate to a weak solution of methyl orange made red with a drop of hydrochloric acid solution. The red colour will disappear, and the more sodium tartrate is added, the more hydrochloric acid must be added to reproduce the red colour. It is a familiar analytical experience that sharp titrations of acids and alkalies are impossible in the presence of weak acids.

The addition to a strong acid of a solution of its salt with sodium diminishes its strength. Sulphuric acid does not act so strongly, for instance, in the presence of sodium sulphate. By dissociating into SO_4'' ions

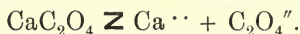


the presence of the salt causes an increase in the concentration of these anions, and according to the equilibrium equation



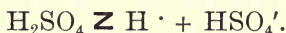
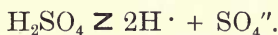
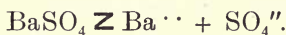
causes a certain number of hydrogen ions to combine into neutral molecules. As before, this produces a diminution of acidity. The weakening effect is not so noticeable as in the case of sodium tartrate and hydrochloric (or sulphuric) acid, and cannot be observed by using an indicator, but it nevertheless exists.

§ 24. *Dissolving of Precipitates.*—The solvent action of acids upon precipitates is usually connected with their hydrogen ions. The solubility of calcium oxalate in hydrochloric acid is a case in point. Like silver chloride, the calcium oxalate is not absolutely insoluble in water. The liquid above, or surrounding the precipitate, must therefore be regarded as a saturated solution with respect to the calcium oxalate. The dissolved calcium oxalate is dissociated thus:—



The addition of hydrochloric acid introduces hydrogen ions, and these remove some of the $\text{C}_2\text{O}_4''$ ions by combining with them to form oxalic acid. More calcium oxalate then dissociates to restore equilibrium and more precipitated calcium oxalate enters into solution to make good the loss. Since oxalic acid is much weaker than hydrochloric acid it is less dis-

sociated, and so the $\text{C}_2\text{O}_4''$ ions are constantly drawn off by the hydrogen ions, supplied by the hydrochloric acid, to form oxalic acid. It is only necessary, therefore, to add a sufficient quantity of hydrochloric acid for all the calcium oxalate to dissolve. Acetic acid does not dissolve calcium oxalate, because acetic acid is much weaker and therefore less dissociated than hydrochloric acid. The stronger (the more strongly dissociated) the solvent acid is relatively to the acid combined in the precipitate, the more powerful is its solvent action. A precipitate like barium sulphate, where the combined acid is comparable in strength with the solvent acid, is not nearly so readily dissolved. Hot and strong hydrochloric acid perceptibly dissolves barium sulphate, but its action is always limited by the dissociation of the sulphuric acid.



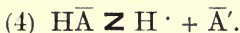
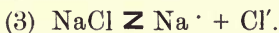
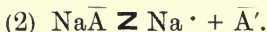
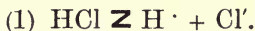
It must be noted that it is not entirely a question of the relative strengths of the free and combined acids. The actual solubility and solubility-product of the precipitate help to determine the course of the reaction. Thus, while strontium and calcium chromates are soluble in acetic acid, barium chromate is insoluble.

The action of acids on metallic sulphides is an important matter for the analyst. The sulphides of

the heavy metals are practically insoluble in water. Their solubility in acids varies, and by the use of dilute acid, metals such as copper may be separated from metals like zinc by the use of sulphuretted hydrogen. The sulphides may be regarded as salts of the weak hydrosulphuric acid (H_2S). As a general rule, therefore, metallic sulphides are soluble in the strong acid hydrogen chloride, just as metallic oxalates are soluble in it. There is, however, considerable variation in the readiness with which hydrochloric acid dissolves the various sulphides. Thus, mercuric sulphide is very insoluble in it, and while copper can be precipitated as sulphide by passing sulphuretted hydrogen through its solution, faintly acidulated with hydrochloric acid, zinc cannot be so precipitated. These facts serve as a reminder that the concentration of the hydrogen ions is not the only factor.

An interesting experiment with zinc sulphate solution serves, however, to indicate the important part played by the concentration of the hydrogen ions in the solvent action of acids upon metallic sulphides. The solution of zinc sulphate is slightly acidulated with hydrochloric acid and sulphuretted hydrogen passed through it. No precipitation of zinc sulphide takes place, but on adding a solution of sodium acetate the white zinc sulphide makes its appearance. This precipitation takes place because the addition of sodium acetate diminishes the concen-

tration of the hydrogen ions. Ignoring the dissociations of the water and dissolved portion of the zinc sulphide and the hydrosulphuric acid, the equations representing the various equilibriums are:—



The acetic acid is much less dissociated than the hydrochloric acid, and (as indicated in equation 4) a diminution in the concentration of the hydrogen ions takes place. This diminution takes place to such an extent that the zinc sulphide can no longer be retained in solution, and it accordingly precipitates.

A very interesting example of the same kind is afforded by the precipitation of the black iron sulphide from acetic acid solution when sodium acetate is added. Iron wire is dissolved in acetic acid and a small portion of the solution treated with sulphuretted hydrogen (a solution of the gas in water is convenient to use for these experiments). On adding sodium acetate solution the black precipitate makes its appearance. In this case the concentration of the hydrogen ions afforded by acetic acid is diminished by adding its own sodium salt. From the two equations

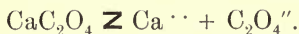


it is evident that the introduction of the anions \bar{A}' into the solution by the dissociation of the sodium acetate increases their concentration. Some hydrogen ions therefore unite with a portion of the \bar{A}' ions to form acetic acid. The reduction in the concentration of the hydrogen ions enables the iron sulphide to come down.

This experiment appears to be a crucial case—deciding between the old way of looking at these reactions and the new. The precipitation of the zinc sulphide on adding sodium acetate to its hydrochloric acid solution was formerly explained by the action of the hydrochloric acid on the sodium acetate to form acetic acid. The comparative weakness of the acetic acid allows the sulphide to come down. This explanation fails in the experiment with the iron acetate.

Similar experiments may be made on the solvent effects of acids on phosphates. Sodium phosphate solution does not precipitate ferric phosphate from ferric chloride acidulated with some hydrochloric acid. Sodium acetate can be added to the solution to so diminish the concentration of the hydrogen ions as to allow the ferric phosphate to come down.

§ 25. *Precipitation and Concentration of Ions.*—For calcium oxalate to remain in the precipitated condition there must be enough C_2O_4'' ions to satisfy the equation—



Hydrochloric acid effects solution by continuously removing the $\text{C}_2\text{O}_4''$ ions, so that their concentration is not enough to precipitate calcium oxalate. Similarly, sulphuretted hydrogen fails to precipitate sulphides when the concentration of S'' ions falls below a certain point. Precipitation is thus dependent on sufficient concentration of the ions concerned being attained.

The precipitation of hydrates of the metals by solutions of caustic alkalies is connected with the concentrations of the hydroxyl ions. The failure of ammonia to precipitate calcium hydrate from solutions of calcium salts, while caustic soda produces the precipitate, is a case in point. Calcium hydrate is somewhat sparingly soluble in water, and according to the equilibrium

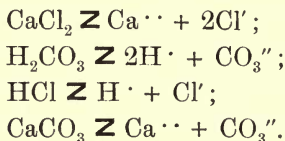


the attainment by the hydroxyl ions in the solution of a certain pitch of concentration might be expected to result in the precipitation of calcium hydrate.

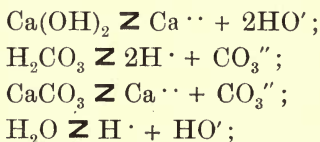
The ionisation of caustic soda is sufficient to produce the necessary concentration, the ionisation of the ammonia into hydroxyl ions is not.

The precipitation of calcium from its solutions as carbonate depends—amongst other things—on the concentration of the CO_3'' ions being great enough. In the case of a solution of calcium hydrate the introduction of carbonic acid gives the necessary pitch of concentration. Carbonic acid will, however,

not precipitate calcium carbonate from a solution of calcium chloride. The equations representing the equilibrium are :—



The comparatively great concentration of the hydrogen ions, due to the ionisation of the hydrochloric acid, removes the CO_3'' ions to such an extent that they fail to attain the concentration necessary for the precipitation of calcium carbonate. In the case of the calcium hydrate, the equations



show how it is possible for the CO_3'' ions to attain the needful concentration. Sodium carbonate solution precipitates chalk from calcium chloride solution, because it dissociates much more than the weak carbonic acid and the CO_3'' ions become sufficiently concentrated.

Calcium carbonate is soluble even in an acid of medium strength like acetic acid, because the hydrogen ions so far retard the ionisation of the carbonic acid as to prevent them from attaining the concentration necessary to precipitate chalk from the solution.

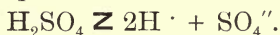
§ 26. *Ionisation and Acid Strength*.—That the relative strengths of acids may be expressed in terms of the degrees to which they are dissociated can be quantitatively shown by means of conductivity and cryoscopic determinations. Cryoscopic determinations comprise estimations of the depression of the freezing points and raising of the boiling points of solutions.

The acids may be arranged in the order of their strengths by various chemical methods. Their capacity to bring calcium oxalate into solution, for instance, may be used for this purpose. Again, two acids in equivalent quantities may be allowed to compete for a base that is not present in sufficient quantity to neutralise all the acid present, and their relative strengths determined by the respective amounts of base obtained by each acid. These and many other methods have been used to arrange the acids in a series according to their strengths. The series so obtained is identical with that obtained by conductivity and cryoscopic methods. Sulphuric acid, for example, is evidently a stronger acid than acetic, and it is accordingly found to be more strongly dissociated. This applies all through the series.

At very great dilution all acids have the same conductivity—that is, they are all equally (because almost completely) dissociated. All acids, therefore, are equally strong when they are very dilute.

Similar reasoning to that employed at the end of paragraph 16 indicates how the complete dissociation of all acids at extreme dilution can be deduced from their equilibrium equations.

Interesting and strong confirmation is thus obtained of the preceding explanations of the weakening of acid effects by the addition of salts of weaker acids. It will have been noticed that in one case, *viz.*, the diminution of the solvent action of acetic acid on iron sulphide, the acid was weakened by the addition of one of its own salts. The solvent action of sulphuric acid on iron sulphide can also be weakened by the addition of its own salts. Potassium and magnesium sulphates produce such a weakening. They do this by introducing SO_4'' ions into the solution and disturbing the equilibrium



This disturbance takes the form of lessening the dissociation of the acid by increasing the concentration of the anions. Since magnesium sulphate has less effect than potassium sulphate it should be less dissociated. Cryoscopic and conductivity determinations confirm this. The salts of divalent metals are, in general, less dissociated than those of the alkali monovalent metals.

Acids, therefore, are less powerful both in the presence of their own salts and of the salts of weaker acids.

From the ionisation point of view, it is now evi-

dent that all fractional precipitations in which acids are employed take advantage of varying concentrations of the hydrogen ions. Barium sulphate can be precipitated in the presence of oxalic acid by taking advantage of the great ionisation of hydrochloric acid. In virtue of the smaller ionisation of acetic acid calcium oxalate can be precipitated in the presence of tartaric acid. The concentration of the hydrogen ions, due to a small amount of hydrochloric acid, is insufficient to prevent the precipitation of mercuric sulphide by sulphuretted hydrogen. If zinc is present, its sulphide comes down on removing the hydrogen ions, by the addition of ammonia, or on considerably diminishing their concentration, by the addition of sodium acetate.

The solvent action of acids upon metals must usually be ascribed to their hydrogen ions. The evolution of hydrogen and formation of zinc chloride when hydrochloric acid acts upon zinc must be so ascribed. Since ionisation of the acid only takes place when dissolved in water or some other dissociating solvent, the pure acid might be expected to be inert towards the metal. It has been shown that liquid hydrochloric acid has practically no solvent action upon metals.

Just as the strengths of acids depend on the extent of their dissociation into hydrogen ions, so the strengths of alkalies depend on the extent of their dissociation in hydroxyl ions.

§ 27. *Nature of Acids and Alkalies.*—Acids and alkalies are substances that when dissolved in some dissociating solvent introduce hydrogen or hydroxyl ions into the solution. It may be here noted that alcohol can exert a dissociative effect on substances dissolved in it. A solution of caustic soda in alcohol has an alkaline reaction. Water, however, is a more powerful dissociating solvent than alcohol.

The question arises as to why certain substances containing hydroxyl groups act as alkalies while others act as acids. Sulphuric acid has the constitution $\begin{array}{c} \text{O} \\ \parallel \\ \text{O} \end{array} \text{S} \begin{array}{c} \text{OH} \\ \diagup \\ \text{OH} \end{array}$ and caustic potash the constitution K—O—H . Both contain hydroxyl groups, but the acid dissociates into hydrogen ions and the potash into hydroxyl ions. The law seems to be that hydroxyl groups united with electro-negative groups yield hydrogen ions, while those combined with positive groups give hydroxyl ions. Potassium is strongly positive, while SO_4 is strongly negative. The hydrogen ions need not necessarily come from hydroxyl groups—those afforded by dissolved hydrochloric acid gas do not. In this latter case the hydrogen is still united with the negative chlorine.

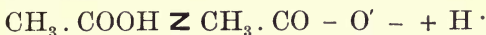
Moreover, the greater the negative or positive character of the anion or cation, the greater the dissociation and the greater the strength of the acid or base. Sulphuric acid is stronger than sulphurous acid and SO_4 is more electro-negative than SO_3 —since

it contains one more atom of the negative oxygen. Similarly, caustic potash and caustic soda are stronger bases than calcium or barium hydrates, and potassium and sodium are more strongly positive than the alkaline earth metals.

An interesting example of the influence of the negative character of the anion in determining the strength of the acid is afforded by acetic acid. This

substance has the constitution
$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{C}-\text{OH} \\ | \quad || \\ \text{H} \quad \text{O} \end{array}$$
 and

dissociates thus:—



The radical $\text{CH}_3-\text{C}(=\text{O})-\text{O}-$ may be made more strongly

negative by introducing three chlorine atoms—which are strongly negative—in the place of three hydrogen

atoms. The resulting acid
$$\begin{array}{c} \text{Cl} \\ | \\ \text{Cl}-\text{C}-\text{C}-\text{OH} \\ | \quad || \\ \text{Cl} \quad \text{O} \end{array}$$
 (trichlor-

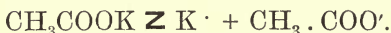
acetic acid) is a much stronger acid than acetic acid itself. In these and numerous other cases it is found that the same principle holds good.

In a similar way, experiments have shown that alkalies dissociate more or less strongly according to the positive nature of their cations.

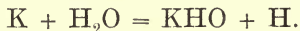
CHAPTER IV.

SOME ELECTROLYTIC AND GENERAL CONSIDERATIONS.

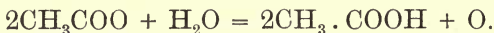
§ 28. *Variations of Electrolytic Products.*—A solution of potassium acetate contains undissociated molecules of the salt, and the ions $K \cdot$ and CH_3COO' produced by electrolytic dissociation.



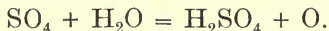
During the electrolysis of the solution the potassium ions travel to the cathode and the anions to the anode. As usual, the discharged cations interact with the water to form potassium hydroxide and hydrogen.



A variety of reactions may take place at the anode. The usual production of acid and oxygen may occur by the action of the water on the discharged anions.



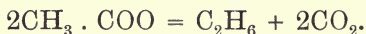
This reaction is of course comparable with the production of sulphuric acid and oxygen at the anode during the electrolysis of sulphuric acid.



This regeneration of acid at the anode is a very

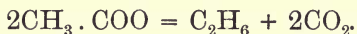
characteristic feature of the electrolysis of acids, though its extent (as will be seen presently) frequently depends upon various circumstances.

In addition to the formation of acetic acid at the anode, ethane and carbon dioxide may result from interactions between the discharged anions.



Other reactions, such as the oxidation of the electrolyte by the electrolytic oxygen and the production of various substances by a variety of reactions in which the discharged anions take part, may occur; but we are here concerned only with the production of acetic acid, ethane and carbon dioxide.

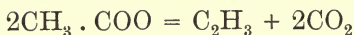
The hydrogen produced at the cathode is a measure of the total decomposition taking place, and the ethane produced at the anode is a measure of the extent of the reaction—



The ratio of ethane to hydrogen is thus a measure of the relative extent to which the latter process takes place.

Obviously, this relative extent will be the greater, the greater is the crowding together at the anode of the discharged anions. This crowding together might be expected to increase with increasing current, since a larger number of anions are discharged per unit time with a greater current than with a smaller. It has been experimentally shown that as the current

increases, the ratio of ethane to hydrogen also increases. A similar increase in the ratio has also been shown to occur when the same current strength is used for solutions of increasing concentration. Lessening the area of the electrode has the effect of increasing the crowding together of the discharged anions. With the same current strength and concentration of solution it would therefore be expected that the less the area of the anode, the greater would be the relative extent of the reaction—



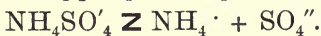
and consequently the greater would be the ratio of ethane to hydrogen. Experiment shows that this ratio does so increase under the above condition.

The actual products obtained during the electrolysis of various substances thus vary with the concentrations of the solutions employed, with the current strength and with the size of the electrodes.

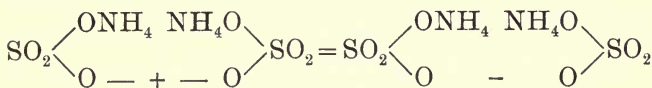
The usual conditions affecting the course of chemical reactions, such as the temperature, also influence the characters and ratios of the products.

The current strength (in ampères) per unit area of electrode is usually termed the current density. It should be noted that if the cathode and anode have different areas the current densities at these two places will be different. As seen above, the current density often considerably influences the nature and yield of the products of the electrolysis.

The importance of the current density is very clearly indicated in the electrolytic preparation of ammonium persulphate. A solution of ammonium sulphate contains undissociated molecules and the ions SO_4'' , $\text{NH}_4 \cdot$ and $\text{SO}_4\text{NH}_4'$.

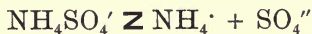


The more the discharged NH_4SO_4 are crowded together at the anode, the greater the production of ammonium persulphate ($(\text{NH}_4)_2(\text{SO}_4)_2$) by their coupling together.



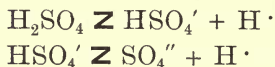
A high current density favours such a crowding, and high current densities are therefore employed in the preparation of persulphates. The temperature must also be kept low to prevent decomposition of the salt when it is formed.

§ 29. *Dissociation in Stages.*—A high concentration of the ammonium sulphate solution is also a favourable condition for the electrolytic preparation of ammonium persulphate. Increasing the concentration of the solution increases the concentration of the $\text{NH}_4\text{SO}_4'$ ions in two ways. In addition to the natural increase, due to the greater total concentration of the salt, the dissociation

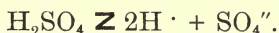


becomes less with increasing concentration. The

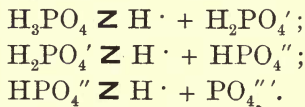
dissociation constant of this second stage of dissociation is much less than that of the first stage. This applies to all substances that dissociate in stages. It applies, for example, to sulphuric acid itself. Sulphuric acid dissociates in two stages—



The latter of these only takes place to any considerable extent when the concentration of the acid in water assumes moderate proportions. It increases, as usual, with increasing dilution, until at low concentration the acid becomes completely (or almost completely) dissociated in the sense—

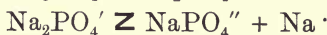
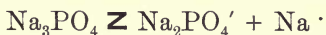


All polybasic acids exhibit this dissociation in stages. Each degree of basicity is represented by a dissociation stage, and the dissociation constants become less and less at each successive stage. Phosphoric acid, for instance, dissociates in the three stages—

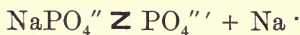


The dissociation constants grow successively less from stage to stage. This implies that the acid strength becomes less and less in the series H_3PO_4 , $\text{H}_2\text{PO}_4'$ and HPO_4'' . The sodium phosphates illustrate this in an interesting way.

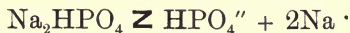
The trisodium salt (Na_3PO_4) is partly converted by solution in water into the disodium salt (Na_2HPO_4) and caustic soda. This can easily be explained by the slight dissociation constant of the third hydrogen atom. The dissociations



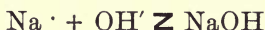
first take place, and then there occurs a slight ionisation in the sense—



The ionisation of HPO_4'' is so slight that the slight dissociation of the water, $\text{H}_2\text{O} \rightleftharpoons \text{HO}' + \text{H} \cdot$, affects the equilibrium. Some of the $\text{H} \cdot$ ions combine with the PO_4''' ions to form HPO_4'' . Further dissociation of the water takes place to restore the equilibrium, and an accumulation of OH' ions takes place to a certain extent. The solution now contains HPO_4'' as well as $\text{Na} \cdot$ ions, and the equilibrium

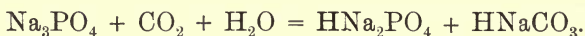


explains the formation of the disodium salt. The presence of the caustic soda in the solution according to the equation

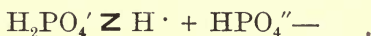


assists in the absorption of carbon dioxide from the air. The formation of sodium carbonate withdraws hydroxyl ions (sodium carbonate acting as a weak

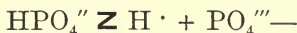
solution of caustic soda as in § 22), and the trisodium phosphate is thus quite converted into the disodium salt :—



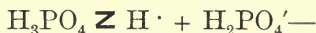
The monosodium salt NaH_2PO_4 reacts acid to phenolphthalein, but not to methyl orange. Since this salt dissociates into sodium ions and $\text{H}_2\text{PO}_4'$ this means that the second stage of dissociation—



corresponds to that of an acid not strong enough to affect methyl orange. The disodium salt Na_2HPO_4 does not affect even phenolphthalein, showing that the third dissociation—



is that of a still weaker acid. This corresponds with the alkaline character of the trisodium salt as noted above. Since phosphoric acid itself is acid to methyl orange the first stage of dissociation—



corresponds to a stronger acid than those represented in the second and third stages.

Substances like barium chloride, containing polyvalent ions, dissociate in stages. As in the case of acids the dissociation constants become less and less from stage to stage. In concentrated solutions the dissociation



is the only one that takes place to any considerable extent. As the concentration becomes less the dissociation



increases, until at great dilution the cleavage into $\text{Ba} \cdot\cdot$ and Cl' is practically complete. Silver nitrate will precipitate all the chlorine from barium chloride solution, if added in sufficient quantity, because by constantly drawing off the chlorine ions to form silver chloride the concentration of the barium chloride constantly diminishes, so that the chlorine is all ultimately ionised and precipitated. Similarly, sulphuric acid will precipitate all the barium from barium chloride, because the constant removal of the $\text{Ba} \cdot\cdot$ ions produces a continuous ionisation until all the barium has been ionised and precipitated.

Ferric chloride dissociates in three stages, and the dissociation constants become successively less. Similar remarks apply to other substances.

§ 30. *Ions and Atoms*.—The discussion of all these reactions in which ions take part indicates great and interesting differences between atoms and ions. It is difficult to realise that a charge of electricity should so completely change the properties of an atom. Perhaps the most marked change of this kind is the solubilising effect. Silver is insoluble in water, but a solution of silver nitrate can contain a considerable amount of dissolved silver ions. It is possible that there is a connection between this

effect and the non-volatility of certain ions like those of chlorine. Chlorine gas can be driven off by heat from its solution in water to a considerable extent. No amount of boiling will drive off the chlorine ions from a solution of sodium chloride. The escape of a negatively charged chlorine ion would leave an excess of positive electricity in the solution, and this would tend to prevent the escape of the chlorine ions. Similarly, the deposition of silver ions from a solution of silver nitrate would leave excess of negative electricity in the solution, and this would tend to prevent the deposition of the silver. In this connection it should be noted that the amount of electricity constituting each charge—corresponding to a valency—is very great when the smallness of the atom is taken into account.

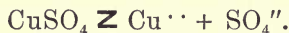
The ions are frequently differently coloured from the atoms. Potassium iodide gives a colourless solution, while iodine gives coloured solutions in alcohol, carbon disulphide and the like. The difference of colour between ferric and ferrous ions is interesting. The yellow colour of the former takes the place of the green of the latter when the ion acquires an extra charge of electricity.

The green colour of potassium manganate solution and the red colour of potassium permanganate solution are connected with the different valencies of, or electric charges on, the anions MnO_4'' and MnO_4' . In this case the higher valency readily changes into the

lower. A solution of potassium manganate (K_2MnO_4) is readily altered by the presence of water into a solution of potassium permanganate (KMnO_4). The difference in colour between the green ion MnO_4^- , and the red ion MnO_4^{+} , readily enables the change into potassium permanganate to be followed when potassium manganate is diluted with water.



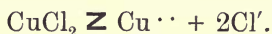
The differences in colour between the ions and molecules show to the eye the changes that take place when copper sulphate is treated with some strong hydrochloric acid and then diluted with water. The solution of copper sulphate is blue. This blue changes to a green tint when strong hydrochloric acid is added, and the blue colour reappears on dilution. The original blue colour is due to the copper ions—



The addition of the hydrochloric acid introduces hydrogen and chlorine ions—



Some copper chloride is produced—



The CuCl_2 molecules are green, and if the Cl^{-} ions introduced by the hydrochloric acid are sufficiently concentrated they are formed in sufficient amount

to render the solution distinctly green. On dilution with water, the CuCl_2 molecules are so much dissociated that the blue colour of the copper ions once more preponderates.

Another noteworthy feature about ions is the rapid nature of the reactions in which they are concerned. The precipitation of silver nitrate by sodium chloride is practically instantaneous. This must be connected with the separate existence of the silver and chlorine ions, and the exact equivalency of their electric charges. Reactions in which ions do not participate are apt to take a much longer time for completion, besides frequently requiring the aid of increased temperature.

§ 31. *Some General Considerations.*—The discussion now about to be concluded has shown that in applying the ionisation conception to the interpretation of chemical reactions it is important to understand the varying degrees of dissociation found in different substances. The very slight dissociation of water is often an important factor. The existence and slight extent of the electrolytic dissociation of water is indicated by the very low electrical conductivity of the pure compound. The ionisation of the various acids and bases must also be kept in mind.

The strong acids comprise the halogen acids (except hydrofluoric) and nitric, chloric, perchloric, sulphuric and the thionic acids.

The hydroxides of the alkalies and alkaline earths are strong bases.

Weak acids are carbonic, silicic, hydrocyanic, boracic and hydrosulphuric.

Ammonia is a moderately strong base; and acetic, sulphurous and phosphoric acids must be classed of medium strength.

Neutral salts are usually the most strongly ionised. The dissociation usually decreases with the valency of the ions, just as in dissociation by stages the ionisation becomes less at each stage. Noteworthy items are the slight ionisation of mercury and cadmium halides. Zinc halides are more strongly dissociated, but less so than most neutral salts.

Hydrogen ions usually tend to reduce the dissociation. Potassium cyanide, for instance, is more dissociated than prussic acid itself.

An application of these principles throws considerable light upon many chemical reactions, and helps to indicate and explain many parallelisms between the electrical and general chemical and physical behaviour of electrolytes.

The above principles have been deduced from the results of numerous chemical reactions and of a large number of cryoscopic and conductivity determinations. The chemical reactions into which substances enter and the products resulting from their decomposition during electrolysis assist in determining the nature of the ions into which they dissociate. Cryoscopic

and conductivity determinations then assist in determining the extent to which they ionise.

Finally, it should be noted that the application of the ionisation hypothesis is in many cases complicated by the formation of complexes by the molecules and ions.



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